

AD669432

25

NRL Report 6667

Neopentyl Polyol Esters for Jet Engine Lubricants—Effect of Tricresyl Phosphate on Thermal Stability and Corrosivity

R. L. COTTINGTON AND H. RAVNER

*Surface Chemistry Branch
Chemistry Division*

February 15, 1968



NAVAL RESEARCH LABORATORY
Washington, D.C.

This document has been approved for public release and sale; its distribution is unlimited.

21

This image shows a blank, aged, cream-colored page, likely an endpaper or flyleaf of a book. The paper has a slightly textured appearance with some minor discoloration and faint smudges, characteristic of old paper. The left edge of the page is bound, showing the stitching or staples of the book's binding. The right edge is slightly irregular. There is no text or other markings on the page.

CONTENTS

Abstract	ii
Problem Status	ii
Authorization	ii
INTRODUCTION	1
EXPERIMENTAL PROCEDURE	2
THERMAL STABILITIES OF NEAT FLUIDS	2
EFFECT OF AMS-5504 STEEL AND TCP ON THERMAL STABILITY	2
Steel Present	4
Steel and TCP Present	6
TCP Present	7
ANALYSIS OF TMP ESTERS 310 AND 312	7
NATURE OF TCP-CONDITIONED METAL SURFACE	7
POLYOL ESTER DECOMPOSITION PRODUCTS	9
INTERACTION OF FREE ORGANIC ACID AMS-5504 STEEL, AND TCP	9
INTERACTION OF TCP, POLYOL ESTERS, AND WATER	10
DISCUSSION	12
SUMMARY	13
CONCLUSION AND RECOMMENDATION	13
FUTURE WORK	14
ACKNOWLEDGMENTS	14
REFERENCES	14

ABSTRACT

Chrome-alloy steel AMS-5504 and mild steel (Specification QQ-S-636) promote thermal decomposition of most neopentyl polyol ester base stocks and some Specification MIL-L-23699 lubricant formulations at 500°F. Without metals, these esters are stable at this temperature. A few such polyol ester base stocks show a much lower sensitivity to steel at 500°F; these exceptions are attributed to the effect of as yet unidentified components.

Tricresyl phosphate (TCP) in 1 to 5 percent concentration effectively stabilizes metal-sensitive polyol esters by passivating the active metal surfaces. As in the case of the diester oils, the combination of TCP and water promotes ester hydrolysis and lead corrosivity; this hydrolytic degradation is inhibited by suitable aliphatic amines.

Work is in progress to determine the effect of (a) phosphorus-containing additives other than TCP, (b) nonphosphorus-containing additives, and (c) metal constitution on the stability and corrosivity of neopentyl polyol esters. The reaction between TCP and monocarboxylic acids is also being investigated.

It is recommended that consideration be given to the inclusion of a more rigorous thermal stability test in Specification MIL-L-23699.

PROBLEM STATUS

This is an interim report; work on this problem is continuing.

AUTHORIZATION

NRL Problem C02-01.301
Project A33-536-501/6521/F012-03-05, NRL 5R002

NRL Problem C02-02.101
Project RR007-08-44-5500

Manuscript submitted November 2, 1967.

NEOPENTYL POLYOL ESTERS FOR JET ENGINE LUBRICANTS — EFFECT OF TRICRESYL PHOSPHATE ON THERMAL STABILITY AND CORROSIVITY

INTRODUCTION

Gas-turbine lubricants conforming to Specification MIL-L-23699 possess desirable properties which have led to their adoption for commercial as well as military aircraft engines. These lubricants, based on esters of neopentyl polyols with aliphatic monocarboxylic acids, are more stable to oxidation than their diester-based MIL-L-7808 predecessors, have higher load-bearing capacities, give cleaner engine operation, and thus permit longer operating times between oil changes and engine overhauls. Esters of neopentyl polyols are also more thermally stable than the diesters because of (a) the absence of a labile hydrogen on the polyol component and (b) the steric protection afforded the molecules by virtue of the shielding of the ester groups in the neopentyl configuration (1). Specification MIL-L-23699 includes a thermal stability requirement, i.e., that the fluid be stable at 500°F for 24 hours in an evacuated Pyrex cell with no metal present. Specification MIL-L-7808 fluids based on esters of dibasic acids cannot meet this requirement.

The trend to gas-turbine engines of more sophisticated design and higher power output, entailing higher bulk oil and bearing temperatures, has added to the already great importance attached to the thermal stabilities of these fluids. For these and related reasons the pyrolysis of esters of different structures has received significant research attention in recent years (2-6).

Reports have recently come to the attention of NavAirSysCom of an occasional corrosion problem encountered in gas-turbine engines of non-Navy aircraft. These engines, of the same type used to power some Navy aircraft, were lubricated with oils similar to those of Military Specification MIL-L-23699 but which had not received military qualification under this specification. The problem centered around corrosive attack on diffuser-case power-shaft struts fabricated from AMS-5504 steel (13 percent chromium). Corrosion generally occurred where large amounts of coke were deposited, and the temperature on occasion reached 500°F or more.

These deposits varied in coherence, but in most instances they were capable of excluding air from contact with oil at the deposit/metal interface. It thus appeared probable that metal corrosion was caused by degradation products generated by thermal, rather than oxidative, breakdown of the lubricant. No formulations found to be corrosive incorporated phosphorus-containing antiwear additives, such as tricresyl phosphate (TCP). As an engineering solution to the problem, the more corrosion-susceptible components of the engines involved are being phosphated to render them less susceptible to attack. No information is available to NRL as to the efficacy of the treatment.

To date, corrosion of the type described has not been reported in Navy aircraft engines lubricated with qualified MIL-L-23699 oils. Nevertheless, it is a matter of concern to NavAirSysCom that the causes of corrosion be determined and preventive measures be devised.

This investigation is concerned with pertinent aspects of the effect of AMS-5504 steel and of TCP on the thermal stability and corrosivity of these lubricants.

EXPERIMENTAL PROCEDURE

Thermal stability and corrosion experiments were conducted at $500^{\circ}\text{F} \pm 2^{\circ}\text{F}$, generally for 96 hours, in evacuated Pyrex cells of the type used in the tests of Specification MIL-L-23699. When metal specimens (either AMS-5504 steel or mild steel, Specification QQ-S-636) were employed in the experiments, the cells were first divided horizontally in two parts, using an emery cutoff wheel. The polished, dried, and weighed specimens (dimensions approximately 75 by 7 by 2 mm) were introduced into the lower segments of the cells, which were then fused to the upper segments. Before use, the cells were simultaneously evacuated and warmed to remove water. Oil samples, generally 5 to 7 ml, were introduced into the cells through the capillary neck using a hypodermic syringe. The sample volume was sufficient to cover the lower half of the metal specimens. Evacuation of the cells and sealing off of the capillary were performed essentially as outlined in the thermal stability test for Specification MIL-L-23699, except that vacuums were of the order of 0.01 mm Hg or less, rather than the specification maximum of 1.0 mm. At the conclusion of the 96-hour heating period, changes in color, viscosity, and acidity of the oil, formation of sediment, weight loss of the metal specimens, and visual evidence of metal corrosion were noted.

Although the main thrust of the investigation was directed toward the behavior of polyol esters, polycarboxylic acid esters and a white petroleum oil were included in the study. The fluids were commercial products, except for two pure esters synthesized at NRL. Before use, the base esters were percolated through alumina and Florisil to remove polar impurities; with one exception lubricant compositions were not so treated because of the probability that additives would be removed. The polyol and acid components of the esters and of the lubricants formulated from them, as determined by NMR and GLC analyses (7,8), are given in Table 1. The esters are identified as to type: P-E, DPE, PE-DPE, and TMP refer to pentaerythritol, dipentaerythritol, pentaerythritol-dipentaerythritol mixtures, and trimethylolpropane esters, respectively.

THERMAL STABILITIES OF NEAT FLUIDS

Thermally induced changes in neutralization number and viscosity of the neat fluids and of formulations in the absence of metals are summarized in Table 2. All polyol ester base stocks and the white petroleum oil were stable under the test conditions. Two lubricant formulations, PE-DPE-319 (both as received and as percolated through adsorbents) and PE-DPE-320, showed only minor viscosity and acidity changes after pyrolysis. The remaining formulations, TMP-315 and PE-DPE-316, developed greater acidities; the former showed a significant viscosity decrease, probably caused by breakdown of the polymeric viscosity-index improver present.

None of the polycarboxylic acid esters examined were thermally stable. By a wide margin, the least stable was triethyl 1,3,5, pentane tricarboxylate (TEPT); the extent of its breakdown may reflect the ability of the short straight chain triethyl ester to form cyclic intermediates and thus promote pyrolysis.

EFFECT OF AMS-5504 STEEL AND TCP ON THERMAL STABILITY

Table 3 summarizes the separate and combined effects on the fluids of AMS-5504 steel and TCP. In these experiments TCP concentration was held at 5 percent; the effect of varying its concentration will be discussed in a later section.

Table 1
Analysis of Neopentyl Polyol Esters

Sample Designation	Mole-Percent of Parent Acids According to Number of Carbons							Av. Acid Chain Length by GLC	Parent Polyols by NMR (mole-%)		
	Iso-C ₅	n-C ₅	n-C ₆	n-C ₇	n-C ₈	n-C ₉	n-C ₁₀	n-C ₁₁	PE	DPE	TMP
Neopentyl Polyol Ester Base Stocks											
Pentaerythritol tetravalerate (PETV)*	0	100	0	0	0	0	0	0	100	—	—
Pentaerythritol tetracaproate (PETC)*	0	0	100.0	0	0	0	0	0	100	—	—
PE-301	0	49.0	13.0	20.0	7.0	11.0	0	0	100	—	—
DPE-303	2.0	58.0	2.0	0	29.0	0	9.0	0	—	100	—
TMP-310	0	0	0.6	2.7	2.8	92.0	1.7	0	—	—	100
TMP-311	3.2	57.0	0.1	0.6	1.6	37.0	1.0	0.2	—	—	100
TMP-312	0	0.5	1.1	92.0	0	4.3	0	0	—	—	100
TMP-313	0	2.7	14.0	18.0	7.4	57.0	1.6	0	—	—	100
PE-DPE-314	20.0	46.0	0	0	2.0	31.0	1.0	0	89	11	—
Neopentyl Polyol Ester Lubricant Formulations											
TMP-315†	0	2.7	14.0	18.0	7.4	57.0	1.6	0	—	—	100
PE-DPE-316†	20.0	46.0	0	0	2.0	31.0	1.0	0	89	11	—
PE-DPE-319	0.5	52.0	0.3	0.3	27.0	19.0	0.6	0	87	13	—
PE-DPE-320	0	83.0	1.0	1.0	11.0	0	4.0	0	73	27	—

*Synthesized at NRL.

†Based on TMP-313.

‡Based on PE-DPE-314.

Table 2
Thermal Stability of Neat Fluids
(96 Hours at 500° F*)

Sample Designation	Neut. No. Incr.	Visc. Change (% at 100° F)
Neopentyl Polyol Ester Base Stocks		
PETV	2.5	-2.0
PETC	0.55	-0.3
PE-301	2.5	-1.5
DPE-303	0.45	-1.0
TMP-310	0.27	-0.4
TMP-311	0.52	-0.5
TMP-312	1.2	-1.1
TMP-313	2.2	-2.1
PE-DPE-314	2.2	-0.9
Neopentyl Polyol Ester Lubricant Formulations		
TMP-315	3.3	-9.9
PE-DPE-316	4.0	-1.7
PE-DPE-319 (as received)	1.5	-3.9
PE-DPE-319 (percolated)	0.75	+1.0
PE-DPE-320	2.6	+3.5
Polycarboxylic Acid Esters		
Bis(2-ethylhexyl)sebacate (DOS)-commercial grade	11.0	-2.2
Diethyl azelate (DOA)-commercial grade	12.0	-5.3
Tris(2-ethylhexyl)1,3,5 pentanetricarboxylate (TOPT)	13.0	-15.0
Triethyl 1,3,5 pentanetricarboxylate (TEPT)	40.0	+37.0
Petroleum Oil		
White petroleum oil (WPO)	0.08	-0.5
Spec. MIL-L-23699 requirement (24-hour test)	2.0 (max)	±5.0

*All results are averages of two or more runs.

Steel Present

In all but two instances, the presence of AMS-5504 steel in the polyol ester base stocks resulted in major degradative changes in at least two of the three usual criteria, i.e., development of acidity, viscosity changes, and corrosive attack on the metal. Corrosion took place both above and below the liquid level but was generally more pronounced in the vapor phase. All esters derived from pentaerythritol, dipentaerythritol, or their mixtures were unstable in the presence of either AMS-5504 or mild steel.

Table 3
Effect of AMS-5501 Steel and Five Percent Tricresyl Phosphate on Thermal Stability of Fluids
(96 Hours at 500°F)

Sample Designation	AMS-5504 Steel Present			AMS-5504 Steel and TCP Present			TCP Present	
	Neut. No. Incr.	Visc. Change (% at 100°F)	Metal Wt. Change (mg/cm ²)	Neut. No. Incr.	Visc. Change (% at 100°F)	Metal Wt. Change (mg/cm ²)	Neut. No. Incr.	Visc. Change (% at 100°F)
Neopentyl Polyol Ester Base Stocks								
PETV	82.	+20.	-7.8	—	—	—	—	—
PETC	88.	+63.	-8.1	0.13	-0.5	< -0.1	—	—
PE-301	102.	+38.*	-9.6	1.2	-0.9	-0.4	—	-0.5
PE-301†	100.	—*	-70.	0.79	-1.0	-0.4	—	—
DPE-303	67.	+21.	-7.0	0.29	-0.5	< -0.1	—	—
TMP-310	0.90	+0.1	-0.9	0.38	+0.9	< +0.1	—	—
TMP-310†	2.4	-3.0	-0.2	—	—	—	—	—
TMP-311	20.	-4.4	-3.7	0.31	+0.5	< -0.1	—	—
TMP-312	1.8	-1.8	-0.3	—	—	—	—	—
TMP-313	56.	-4.2	-5.2	3.5	-2.5	-0.2	—	—
PE-DPE-314	79.	+6.9	-7.1	1.7	+0.7	< +0.1	1.7	+0.7
Neopentyl Polyol Ester Lubricant Formulations								
TMP-315	48.	+9.9	-11.	4.1	-7.2	< +0.1	2.5	-6.9
PE-DPE-316	3.8	-1.2	< +0.1	—	—	—	—	—
PE-DPE-319 (as received)	18.	+0.5	-3.4	2.2	-3.3	< +0.1	—	—
PE-DPE-319 (percolated)	§	§	-52.	0.62	+1.4	< +0.1	0.57	+0.9
PE-DPE-320	3.5	-1.3	-0.3	2.2	-0.1	-0.1	—	—
Dicarboxylic Acid Esters								
DOS	4.3	-6.2	-0.1	49.7	+38.	+0.3	42.	-4.9
DOA	5.2	-9.8	-0.2	111.	-40.	+0.4	108.	-49.
Petroleum Oil								
WPO	0.13	-0.1	< +0.1	—	—	—	0.1	+0.2

*One of duplicate runs exploded.

†Mild steel substituted for AMS-5504.

‡120-Hour run.

§Fluid semisolid.

¶In a duplicate run, sample essentially converted to yellow solid. Crystals identified as sebacic acid.

Although the neutralization number increases of PE-301 were comparable in the presence of the two steels, corrosion of the mild steel was 7 times greater than that of the AMS-5504. The two base stocks not adversely affected by AMS-5504 steel were TMP-310 and TMP-312, with average unbranched acid chains of 8.9 and 7.1 carbon atoms, respectively (see Table 1). In contrast, TMP-311 and 313, with average acid chain lengths of 6.6 and 8.1 carbon atoms, respectively, evidenced gross deterioration. Of the TMP esters, only TMP-311 contained some branched C_5 acid.

In view of the instability in the presence of AMS-5504 steel of all the PE and DPE esters and of two TMP ester, the stabilities of TMP base stocks 310 and 312 were unexpected. Increasing the exposure time of TMP-310 to 120 hours did not materially affect its stability (see Table 3). Apparently the better stabilities of TMP-310 and 312 are due to factors other than marginal exposure times.

There was no improvement with steel present in the thermal stability of lubricant formulation TMP-315 over that of its base stock TMP-313. On the other hand, formulation PE-DPE-316 was considerably more stable than its base stock precursor PE-DPE-314. Formulation PE-DPE-320 was also stable, but no base stock was available with which to compare it. It may be noted that stable formulations PE-DPE-316 and 320 contained organic phosphorus compounds as antiwear additives and that PE-DPE-319 did not.

Percolating formulation PE-DPE-319 through alumina and Florisil worsened the already poor thermal stability of the "as received" material (Table 3). It is possible that the adsorbents removed some effective polar material which did not contain phosphorus, since this element was absent from the formulation.

Pyrolysis of the two dicarboxylic acid esters, a sebacate and an azelate, in the presence of AMS-5504 steel led to the same extensive degradation found when steel was absent (see Table 2). A considerable quantity of sediment, probably free dibasic acid, was formed in both fluids.

No adverse effect on the stability of the petroleum oil appeared with AMS-5504 metal present.

Steel and TCP Present

Table 3 also lists the effect on thermal stabilities when both AMS-5504 steel and TCP (5 weight-percent) are present. In every instance in which the base stock polyol esters and lubricant formulations had previously evidenced serious degradation with the metal present, the addition of TCP resulted in spectacular improvement. Similar improvement due to TCP was obtained with PE-301 when mild steel was substituted for AMS-5504 steel.

In sharp contrast to its beneficial effect on polyol esters, addition of TCP to the two dicarboxylic acid esters with AMS-5504 steel present resulted in their catastrophic degradation. A large quantity of sebacic acid was present in DOS at the conclusion of the run; in DOA the material was presumed to be azelaic acid. Despite the high temperature and the large concentration of free acid, little attack on the metal specimens occurred, confirming the experience of other investigators (5). This inertness may be accounted for by the fact that metal salts of dicarboxylic acids formed at the metal/oil interface are only slightly soluble in the esters and would therefore serve as protective coatings. This phenomenon had been shown in an earlier study (9) to account for the inertness of lead immersed in MIL-L-7808-type esters with free dicarboxylic acids present.

TCP Present

The effect of TCP on thermal stability in the absence of metal was determined by additions of the phosphate to selected neat fluids (Table 3). Two polyol ester base stocks, two polyol ester formulations, and the petroleum oil were examined. All were as stable as the original fluids (compare with Table 2). When TCP was added to the dicarboxylic acid esters, however, more serious degradation occurred than had been the case with the neat fluids.

ANALYSIS OF TMP ESTERS 310 AND 312

From the data reported above, the ability of TCP (and possibly certain other organic phosphorus-containing compounds) to stabilize polyol ester-steel systems against thermal degradation is clearly delineated. In the case of the two base stock TMP esters 310 and 312, which were stable with metal exposure, the presence of a phosphorus-containing material was at first suspected. Analysis of the phosphorus content of one of the fluids, TMP-310, revealed only 0.002 percent phosphorus to be present, or 0.01 percent calculated as TCP. As will be shown in the following section, this amount would be too low a concentration to have any beneficial effect on the system. In addition, NMR, GLC, and IR analyses of both fluids not only confirmed the absence of phosphorus compounds but also confirmed the absence of other impurities in detectable concentrations.

NATURE OF TCP-CONDITIONED METAL SURFACE

In the experiments described above, a 5-weight-percent concentration of TCP was used. To determine the limiting effective concentration of TCP, experiments were made with several lower concentrations in PE-301. Results are shown in Table 4. Substantial improvement in stability and decreased corrosivity of the fluid were obtained with 0.5 and 1.0 percent of the phosphate but not with 0.1 percent. It would thus appear that TCP concentrations at least 1.0 or 2.0 percent would be required to improve significantly the stability of the polyol esters under the pyrolysis test conditions employed here.

Table 4
Effect of Tricresyl Phosphate Concentration on Thermal
Stability of a PE-301-AMS-5504 Steel System
(96 Hours at 500° F)

TCP (%)	Neut. No. Incr.	Visc. Change (% at 100° F)	Metal Wt. Change (mg/cm ²)
None	102.	+38.	-9.6
0.1	51.	+8.0	-5.3
0.5	2.5	-1.6	-0.8
1.0	1.6	-2.5	-0.7
5.0	1.2	-0.9	-0.4

The effect of TCP-pretreated steel on the thermal stability of the polyol esters was also studied. A specimen of AMS-5504 steel was immersed in base stock ester TMP-313 containing 5 percent TCP and then exposed to 500° F (Table 5, Run 2). At the conclusion of the run, the specimen predictably showed little weight loss and the fluid only minor property changes. The solvent-cleaned specimen was then transferred to a fresh cell charged with sufficient neat TMP-313 to cover the lower half of the specimen, and the pyrolysis experiment repeated. As shown in Run 3, the metal and fluid were virtually unaffected. When these results (Run 3) are compared with those of Run 1 using untreated steel, the improvement due to the TCP pretreatment is indeed impressive.

Table 5
Effect of TCP-Conditioning Treatments of AMS-5504 Steel on Thermal
Stability of Neopentyl Polyol Base Stock Ester TMF-313
(96 Hours at 500° F)

System	Neut. No. Incr.	Visc. Change (% at 100° F)	Metal Wt. Change (mg/cm ²)
1. No TCP*	48.	-5.2	-4.6
2. 5% TCP*	2.5	-2.2	<+0.1
3. No TCP†	4.2	-1.9	-0.1
4. No TCP‡ (after abrasion)	12.	-3.1	-1.3
5. Phosphoric acid pretreatment§	24.	-8.9	-1.9
6. Phosphoric acid pretreatment¶	17.	-5.8	-1.5

*Steel specimen completely immersed in fluid.

†TCP-conditioned steel specimen from Run 2. Half of specimen immersed in neat fluid.

‡TCP-conditioned steel specimen from duplicate of Run 2. One flat side of specimen abraded with 240-grit silicon carbide paper after exposure to TCP. Lower half of specimen immersed in neat fluid.

§Steel specimen pretreated with warm dilute H₃PO₄ (1:2) for 5 minutes; 94-hour test.

¶Steel specimen pretreated with warm dilute H₃PO₄ (1:2) for 15 minutes; 94-hour test.

In a collateral experiment, Run 4, one side of a TCP-treated steel specimen was lightly abraded, transferred to a fresh cell, half immersed in neat TMP-313 fluid, and pyrolyzed. Metal weight loss and fluid degradation were intermediate between those obtained when untreated and TCP-treated metals were exposed to the neat fluid (Runs 1 and 2). Corrosive attack on the metal was most evident on the abraded portion exposed to hot vapor. When AMS-5504 steel was pretreated with hot, dilute phosphoric acid, rinsed thoroughly with distilled water, dried, and then exposed to TMP-313 at 500° F (Runs 5 and 6), degradation of the fluid and corrosive attack on the metal were also intermediate between the results obtained when TCP-treated and untreated metals were present.

Formation of phosphate layers on metal substrates in the presence of TCP has been reported by other workers (10-12). Whatever is the nature of the TCP-treated metal surface, at least as regards the effect on ester thermal stability, it is not duplicated by brief exposure to phosphoric acid. To gain some insight as to whether, under the conditions of the present experiments, TCP promotes the formation of a phosphorus-containing film on the metal surface analogous to that obtained by other methods (13-15), AMS-5504 steel specimens were exposed at 500° F to both neat TCP and to base stock TMP-313 containing 5 percent TCP, cleaned with hot solvent, and treated with hot dilute nitric acid for a few minutes. Activation analysis of the dried-acid extracts showed similar phosphorus contents, 160 and 200 γ , respectively. By way of comparison, the acid extract from a reference metal specimen which had not been exposed to TCP contained only 40 γ of phosphorus. While this increase in the surface-phosphorus contents of metals exposed to hot TCP is significant, it does not prove that the protection observed is the result of a phosphate-containing coating. Neither x-ray nor electron-diffraction analyses of the TCP-treated metal showed a crystalline phosphorus-containing deposit; a phosphate deposit on the metal substrate, however, would probably be thin and amorphous (15).

Electron-diffraction analysis, nevertheless, did reveal the presence of a thin film whose pattern approximated that of a spinel. Spinel is a lattice structure incorporating mixed metal oxides which may, in certain instances, impart corrosion resistance to the metal substrates to whose surfaces they are bonded (13). Diffraction studies of a reference, unused AMS-5504 steel specimen showed a partial spinel pattern indicating a thinner

layer than that observed when the metal had been exposed either to neat, thermally unstable TMP-313 or to the TCP-stabilized fluid. Thus, a thin spinel film alone does not prevent thermal decomposition of the oil or corrosive attack on the metal, but the data are insufficient to show whether a heavier spinel film contributes to the reduced interaction between metal and oil in the presence of TCP.

POLYOL ESTER DECOMPOSITION PRODUCTS

Three base stock TMP esters (310, 311, and 312) and two PE-DPE-based formulations (315 and 319) were pyrolyzed under various conditions, and the free acids evolved were analyzed by GLC. As shown in Table 6, the acids were generated in about the same proportions as they were present in the original fluids (see Table 1) regardless of whether the fluids were pyrolyzed neat or with metal and/or TCP present. The main discrepancy was in TMP-312 in which the C₉ acid, originally present in 2.4-mole-percent concentration, was not detected after pyrolysis. No conclusions about the structure of the ester fragments remaining after loss of the acidic components could be established from infrared analysis.

Table 6
Free Carboxylic Acids Generated by Pyrolysis of Neopentyl
Polyol Esters in Presence of AMS-5504 Steel
(96 Hours at 500°F)

Sample	Parent Acids (mole-%)							
	Iso-C ₅	C ₅	C ₆	C ₇	C ₈	C ₉	C ₁₀	C ₁₁
TMP-310	0	0	0.5	3.0	3.2	91.	2.1	0
TMP-311	2.9	55.	0.1	0.6	1.5	39.	0.7	0
TMP-315	0	2.8	14.	19.	7.6	55.	1.5	0
PE-DPE-319*	0	58.	0	0	24.	18.	0	0
PE-DPE-319†	0.7	55.	0	0	26.	18.	0	0
TMP-312*	0	0	0	96.	0	0	4.0	0

*Neat fluid only.

†AMS-5504 steel and 5% TCP present during pyrolysis.

INTERACTION OF FREE ORGANIC ACID, AMS-5504 STEEL, AND TCP

The component monocarboxylic acids of the esters studied in this program are of intermediate strength, K_a ca. 10^{-5} , and their ultimate fate after their thermally induced regeneration in the systems described is of interest. The reactions of valeric acid (5 weight-percent in the stable petroleum oil) were studied at 500°F with TCP and/or AMS-5504 steel present. The results in Table 7 are corrected for the unavoidable loss of valeric acid by volatilization during the preliminary sample preparation procedure. Insignificant changes occurred when samples of valeric acid in the petroleum oil were pyrolyzed. In the presence of AMS-5504 steel, however, the neutralization number decreased from 20 to 1, and the viscosity increased 6.9 percent, indicating the loss of valeric acid. The quantity of acid consumed can be approximately accounted for by the weight loss of the metal specimen, assuming that the ferrous salt was formed. Addition of TCP to the AMS-5504 steel-valeric acid-petroleum oil system caused changed similar to those encountered in the absence of TCP. Evidently TCP does not react with the metal surface to form a protective coating when an initially large concentration of monocarboxylic acid is present.

Table 7
Interaction of Valeric Acid, Tricresyl Phosphate,*
and AMS-5504 Steel in White Petroleum Oil (WPO)
(96 Hours at 500° F)

Additive in WPO	Orig. Neut. No.	Final Neut. No.	Visc. Change (% at 100° F)	Metal Wt Change (mg/cm ²)
None	0.01	0.09	-0.5	—
AMS-5504	0.01	0.14	-0.1	+0.1
TCP	0.01	0.11	+0.2	—
5% valeric acid†	20.	21.	+1.0	—
AMS-5504 + 5% valeric acid	20.	1.0	+6.3	-2.6
AMS-5504 + TCP + 5% valeric acid	20.	3.0	+7.1	-4.3

*TCP in 5-weight-percent concentration when present.

†A blank run in which 5 percent of valeric acid in mineral oil was evacuated while sealed in a glass tube showed a reduction in neutralization number from 26 to 20 and a viscosity increase of 2.5 percent at 100° F. The last three entries in the table have been corrected for these changes.

In another series of experiments, it was found that heating a mixture of TCP and valeric or other monocarboxylic acid can result in a net increase in acidity, including a strong acid component. This reaction and its practical implications are being investigated and will be reported at a later date.

INTERACTION OF TCP, POLYOL ESTERS, AND WATER

In an earlier study (9) on the storage stability and lead corrosivity of oils based on dibasic acid esters (Specification MIL-L-7808) it was concluded that: (a) corrosion was caused by the generation of acidic half esters resulting from hydrolysis of diesters during long-term storage, (b) the hydrolysis reaction was normally slow unless catalyzed by TCP, (c) the activity of TCP was due either to its own strongly acid hydrolysis products or to acidic impurities, and (d) dissolved water was a requisite for all of these reactions to occur. It was also shown that aliphatic amine additives which neutralized the TCP-derived acids stabilized the diester-TCP system against catalyzed hydrolysis. Although the effect of TCP on the hydrolysis and lead corrosivity of polyol esters is not directly related to the main point of the present investigation, it is pertinent to the problem of oil stability, particularly since the solubility of water in the polyol esters is about three times greater than in the diesters of Specification MIL-L-7808-type lubricants.

Specifications MIL-L-7808 and MIL-L-23699 permit qualifying oils to have a maximum lead corrosion number of 6 mg/in.². To assure adequate storage stability, lead-corrosion losses may not exceed 25 and 150 mg/in.² after 48 and 168 hours, respectively, at 185° F. In the present study the storage test was further accelerated by raising the test temperature to 230° F. PE-301 containing 0.01 percent water and 1.0 percent phenyl- α -naphthylamine as the antioxidant was the reference fluid. The effects of added water, TCP, and an aliphatic amine (2,6-ditertiarybutyl- α -dimethylamino-p-cresol) on the storage stability of the reference polyol are shown in Table 8.

There were no significant changes in water content, acidity, or corrosiveness of the reference fluid (Run A) after 168 hours. Raising the water content to 0.17 percent (Run B) caused only a minor increase in corrosion. A somewhat greater lead weight loss was observed after the addition of "as received" TCP to the reference fluid (Run C).

Table 8
Effect of Water and TCP on the Lead Corrosivity of Base
Stock Ester PE-301 After Storage at 230°F*

Run	Additions to PE-301	H ₂ O Content			Neut. No.			Lead Corrosion No.		
		% (orig.)	48 Hr	168 Hr	Orig.	48 Hr	168 Hr	Orig.	48 Hr	168 Hr
A	None	0.01	0.01	0.02	0.01	nil	0.03	1.4	0.8	0.1
B	Water	0.17	—	0.16	0.01	nil	0.05	—	0.5	11.0
C	TCP (as rec'd)	0.01	0.02	0.01	nil	0.02	nil	—	2.5	21.0
D	TCP (as rec'd) + water	0.22†	0.01	0.01	0.02	3.0	8.2	—	255.	216.
E	TCP (perc'd)† + water	0.22†	0.15	0.06	0.02	0.03	4.3	—	2.3	207.
F	TCP (as rec'd) + water + amine‡	0.21	—	0.21	0.02	0.02	0.46	—	0.1	41.

*All samples contain 1 percent phenyl- α -naphthylamine. When present, TCP is in 5-weight-percent concentration.

†Estimated value.

‡Percolated through activated alumina and Florisil.

§One percent, 2,6-ditertiarybutyl- α -dimethylamino-p-cresol.

With the addition of both "as received" TCP and water to the reference fluid, almost all of the water was consumed in the first 48 hours, and the corrosion number was well above 200, Run D. The effects of acidic and polar impurities, originally present in TCP, upon the reference fluid in the presence of water are shown by comparing Runs D and E. In the latter experiment the TCP was percolated through alumina and Florisil prior to its incorporation into the fluid; the result was a significantly longer induction period than in Run D before major degradative changes were apparent. In Run F, which differed from Run D only by the addition of 1.0 percent of 2,6-ditertiarybutyl- α -dimethylamino-p-cresol, the water content was unchanged after 168 hours, the neutralization number had increased to only 0.46, and the lead corrosion number was only one-fifth that of Run D.

It is evident that: (a) the mechanisms responsible for the effect of TCP on the corrosiveness developed in diester oils during storage also govern the deterioration of polyol ester-base oils and (b) aliphatic amines effectively reduce or eliminate the catalytic activity of the acid phosphates by reacting with them. It should be recalled, however, that experience with the aliphatic amine additive (2,6-ditertiarybutyl- α -dimethylamino-p-cresol) has shown that it reacts with certain dicarboxylic acids to form products insoluble in Specification MIL-L-7808 oils (9). Until it has been determined that this amine additive is compatible with other additives and the monocarboxylic acids generated from polyol esters in Specification MIL-L-23699 oils, its use is not recommended.

The interaction of TCP, water, and polyol esters with AMS-5504 steel was also studied at 500°F. One drop (0.5 to 0.6 weight-percent) of water was added to cells containing TCP and AMS-5504 steel specimens in base stocks PE-301 and TMP-310. After exposure for 96 hours, the cell contents were examined. Table 9 shows that the results of the experiments were inconclusive; water appeared to be consumed in hydrolysis of the esters, but corrosion of the steel occurred in only one of the two samples, PE-301.

Table 9
Effect of TCP* and Water† on the Corrosiveness of
Neopentyl Polyol Esters to AMS-5504 Steel
(96 Hours at 500°F)

Sample	Neut. No. Increase	Visc. Change (% at 100°F)	Metal Wt. Change (mg/cm ²)
PE-301	5.0	-1.5	-1.7
TMP-310	12.	-2.5	+0.1

*5 weight-percent.

†0.5 to 0.6 weight-percent.

DISCUSSION

The data presented reveal a number of significant findings, some of which in turn raise other questions:

1. All neopentyl polyol esters studied were stable to pyrolysis at 500°F. They were, for the most part, readily degraded when bulk chrome alloy or mild steel was present, but two exceptions have been noted, both being trimethylolpropane esters. Analysis has thus far not revealed whether impurities in either the stable or unstable esters account for their diverse behavior. From the data, however, the weight of evidence indicates that carefully synthesized and purified laboratory preparations, such as PETV and PETC, are thermally unstable with the metal present; thus, it may be surmised that unidentified trace impurities account for the anomalous stability of the two TMP esters. Additional work will be necessary before definite conclusions can be drawn.

2. The role of TCP in reducing the degradative catalytic effect of steel during polyol ester pyrolysis is probably complex. Either one or a combination of two mechanisms might explain its activity: (a) formation of an inert metal phosphate film and (b) enhancement or refinement of the air-oxidized spinel structure already on the metal surface to augment its inertness to acidic attack. At the present stage of this investigation, no final choice can be made between these hypotheses.

3. The thermal stability of neat polycarboxylic acid esters at 500°F is perceptibly less than that of polyol esters. Although bulk steel catalyzes degradation of the polycarboxylic acid esters, as it does also that of most polyol esters, TCP does not provide the stabilizing effect in the former esters that it does in the latter. It is known that minor concentrations of TCP hydrolysis products or acidic impurities catalyze hydrolysis of polycarboxylic acid esters; the present work indicates that either TCP or such acidic impurities may also catalyze thermal breakdown of these esters.

4. When AMS-5504 steel (and probably other classes of steel) are pretreated with TCP, the metal does not, thereafter, catalyze thermal breakdown of polyol esters nor is it corroded by these fluids at 500°F. In practice, however, such protective treatment may not by itself be effective in all components of gas-turbine engines, since abrasion of the treated metal during engine operation could then expose a fresh catalytically active surface. There is a strong possibility, however, that the abraded area would be "healed" if TCP were a component of the lubricant formulation.

5. Specification MIL-L-23699 polyol ester-based lubricants are sensitive to the same general type of degradative effects of TCP and water during long-term storage as

are the diester lubricants of Specification MIL-L-7808. Since at present, use of a break-in sacrificial lead coating on bearings in aircraft jet engines is being eliminated, this sensitivity may not be significant. One conclusion in Ref. 9 stated that "the most positive and generally applicable method for assuring long storage life is to package dry MIL-L-7808 oils in dry cans"; the same can probably be stated for MIL-L-23699 oils.

SUMMARY

A study was made of the thermal stability at 500° F of neopentyl polyol ester base stocks and lubricant formulations derived from trimethylolpropane (TMP), pentaerythritol (PE), dipentaerythritol (DPE), and mixtures of the latter two; four polycarboxylic acid esters and a white petroleum oil were also examined. The effects of TCP, AMS-5504 chrome alloy steel, and mild steel (Specification QQ-S-636) were determined.

All neat base stocks and all but one lubricant formulation (which contained a polymeric viscosity index improver) were thermally stable under the experimental conditions. No polycarboxylic acid ester was stable; the petroleum oil was not affected. With AMS-5504 steel or mild steel present, seven of the nine base stocks (including two laboratory-synthesized, highly purified PE esters) underwent serious degradation and became corrosive, but two TMP base stock esters were virtually unaffected. Of the formulated oils only those containing TCP or other phosphorus-containing additives were stable and non-corrosive. Percolation through active adsorbents of one unstable formulation (no phosphorus compound present) rendered the fluid even less stable. The stability of petroleum oil was unaffected by the presence of steel.

With steel present, 1 to 5 percent of TCP markedly improved the thermal stabilities of those polyol ester base stocks and formulations which had been adversely affected by the metal alone.

By itself, TCP did not impair the intrinsic stabilities of the polyol esters or the petroleum oil, but it increased the breakdown of the dicarboxylic acid esters.

AMS-5504 steel pretreated at 500° F with TCP was rendered passive and did not, thereafter, catalyze breakdown of otherwise susceptible polyol esters, provided the metal surface remained intact.

Free monocarboxylic acids were generated by pyrolyzed polyol esters in the same proportions as they occurred in the parent fluids. The molecular structure of the residual portions of the esters could not be determined. Acids regenerated from dicarboxylic acid esters were less corrosive than monocarboxylic acids, probably because their reaction products with steel formed protective films.

Under accelerated storage conditions, neat polyol esters containing small amounts of water were relatively stable to hydrolysis. The combination of TCP and water accelerated hydrolysis, resulting in acids corrosive to lead. Prior removal of acidic impurities or breakdown products of TCP by adsorbents delayed, but did not prevent, a degradative catalytic effect. Aliphatic amines which react with TCP-derived acids markedly reduced the catalyzed hydrolysis of the esters.

CONCLUSION AND RECOMMENDATION

It is concluded that TCP, and possibly certain other phosphorus-containing compounds, exert a marked beneficial effect on the thermal stability of polyol esters used in Specification MIL-L-23699 formulations by passivating the active catalytic surfaces of AMS-5504 and mild steels.

It is recommended that the thermal stability requirement of Specification MIL-L-23899 be modified so as to include the presence of steel (mild, AMS-5504, or other appropriate alloy) and that exposure time at 500° F be increased from the present 24 hours to at least 72 hours.

FUTURE WORK

1. A further effort is being made to resolve the anomaly of the two TMP esters which were found to be stable in the presence of steel at 500° F.
2. The effect of phosphorus-containing additives other than TCP and of other classes of additives on the thermal stability and corrosivity of neopentyl polyol esters is being investigated.
3. Additional work is being done to determine the nature of the protective film formed on steel in the presence of TCP in a polyol ester.
4. The effect of alloying constituents of steel and of soluble metal salts on thermal stability and corrosivity of the polyol esters is being investigated.
5. The reaction between TCP and monocarboxylic acid is being investigated.

ACKNOWLEDGMENTS

The assistance given by (a) Mr. C. M. Murphy, Code 6170, Chemistry Division, through his generous advice and comments in the course of the investigation, (b) Dr. M. C. Bloom, Code 6107, Chemistry Division, through general discussions of corrosion phenomena, (c) Dr. Robert Jones, Code 6160, Chemistry Division, for electron-diffraction data, (d) Miss D. S. Cain, Code 6110, Chemistry Division, for infrared spectroscopy data, and (e) Code 6370, Metallurgy Division, in performing some of the analyses is acknowledged with thanks.

REFERENCES

1. Critchley, S.W., and Miles, P., "Synthetic Lubricants - Selection of Ester Types for Different Temperature Environments," presented at Industrial Lubrication Symposium, London, March 1965
2. Allen, R.J.P., Forman, R.L., and Ritchie, P.D., J. Chem. Soc., 2717, 1955
3. Durr, A.M. Jr., Meador, W.R., and Thompson, C.E., ACS Petrol. Div. Preprints 8 (No. 3):49 (Sept. 1963)
4. Golomb, A., and Ritchie, P.D., J. Chem. Soc., 4515, 1958
5. Klaus, E.E., Tewksbury, E.J., Fenske, M.R., et al., Petroleum Refining Laboratory, The Pennsylvania State University, Air Force Materials Laboratory Technical Report AFML-TR-67-107 Part 1 (Mar. 1967)
6. Ritchie, P.D., J. Oil and Colour Chemists Assoc., 659, 1962
7. Moniz, W.B., and Poranski, C.F., Jr., "NMR Analysis of Mixed Pentaerythritol-Dipentaerythritol, and 1,1,1-Trimethylolpropane Esters," NRL Report 6307, Aug. 19, 1965

8. O'Rear, J.G., and Sniegowski, P.J., "Analysis for Acyl Components of Neopentyl Polyol Ester Lubricants," NRL Report 6338, Jan. 5, 1966
9. Murphy, C.M., Ravner, H., and Timmons, C.O., J. Chem. Eng. Data 6:135 (1961)
10. Barcroft, F.T., and Daniel, S.G., Trans. ASME Ser. D, J. Basic Eng. 87:761 (1965)
11. Godfrey, D., ASLE Trans. 8:1 (1965)
12. Klaus, E.E., and Bieber, H.E., ASLE Trans. 8:12 (1965)
13. Bloom, M.C., and Strauss, M.B., "Steel Corrosion Mechanisms Under Conditions Pertinent to Steam Power Generation," NRL Report 5427, Dec. 30, 1959
14. Kruger, J., and Bloom, M.C., Ind. Eng. Chem. 48:1354 (1956)
15. Maher, M.F., "Phosphate Coatings," Chapter in "Metal Finishing Guidebook Directory, 1967," Westwood, New Jersey:Metals and Plastics Publications, Inc.

DOCUMENT CONTROL DATA - R & D

(Security classification of title, body of abstract and indexing annotation must be entered when the overall report is classified)

1. ORIGINATING ACTIVITY (Corporate author) Naval Research Laboratory Washington, D.C. 20390		2a. REPORT SECURITY CLASSIFICATION Unclassified	
		2b. GROUP	
3. REPORT TITLE NEOPENTYL POLYOL ESTERS FOR JET ENGINE LUBRICANTS -- EFFECT OF TRICRESYL PHOSPHATE ON THERMAL STABILITY AND CORROSIVITY			
4. DESCRIPTIVE NOTES (Type of report and inclusive dates) This is an interim report; work is continuing.			
5. AUTHOR(S) (First name, middle initial, last name) R.L. Cottingham and H. Ravner			
6. REPORT DATE February 15, 1968		7a. TOTAL NO. OF PAGES 20	7b. NO. OF REFS 15
8a. CONTRACT OR GRANT NO. NRL Problems C02-01.301 & C02-02.101 b. PROJECT NO. A33-536-501/6521/F012-03-05, NRL 5R002 RR007-08-44-5500 d.		9a. ORIGINATOR'S REPORT NUMBER(S) NRL Report 6667	
		9b. OTHER REPORT NO(S) (Any other numbers that may be assigned this report)	
10. DISTRIBUTION STATEMENT This document has been approved for public release and sale; its distribution is unlimited.			
11. SUPPLEMENTARY NOTES		12. SPONSORING MILITARY ACTIVITY Department of the Navy (Naval Air Systems Command and Office of Naval Research), Washington, D.C. 20360	
13. ABSTRACT <p>Chrome-alloy steel AMS-5504 and mild steel (Specification QQ-S-636) promote thermal decomposition of most neopentyl polyol ester base stocks and some Specification MIL-L-23699 lubricant formulations at 500°F. Without metals, these esters are stable at this temperature. A few such polyol ester base stocks show a much lower sensitivity to steel at 500°F; these exceptions are attributed to the effect of as yet unidentified components.</p> <p>Tricresyl phosphate (TCP) in 1 to 5 percent concentration effectively stabilizes metal-sensitive polyol esters by passivating the active metal surfaces. As in the case of the diester oils, the combination of TCP and water promotes ester hydrolysis and lead corrosivity; this hydrolytic degradation is inhibited by suitable aliphatic amines.</p> <p>Work is in progress to determine the effect of (a) phosphorus-containing additives other than TCP, (b) nonphosphorus-containing additives, and (c) metal constitution on the stability and corrosivity of neopentyl polyol esters. The reaction between TCP and monocarboxylic acids is also being investigated.</p> <p>It is recommended that consideration be given to the inclusion of a more rigorous thermal stability test in Specification MIL-L-23699.</p>			

14 KEY WORDS	LINK A		LINK B		LINK C	
	ROLE	WT	ROLE	WT	ROLE	WT
Corrosion Steel Gas-turbine engines Pyrolysis Phosphates Spinel structure Thermal stability Lubricants, gas-turbine engine Lubricants, polyol ester						